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(12) (19) (CA) **Demande-Application**

(21) (A1) **2,247,662**
(22) 1998/09/18
(43) 1999/03/22

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(51) Int.Cl.[6] C07C 317/18, C07C 67/42, C07C 51/285, C07C 303/16, C07C 315/02
(30) 1997/09/22 (19741645.4) DE

(54) **PROCEDE ET APPAREILLAGE POUR L'OXYDATION DE COMPOSES ORGANIQUES EN PHASE LIQUIDE A L'AIDE DE PEROXYDES**

(54) **PROCESS AND APPARATUS FOR THE OXIDATION OF ORGANIC COMPOUNDS IN LIQUID PHASE USING PEROXIDE OXIDIZING AGENTS**

(57) On oxyde le composé organique en solution en ajoutant un peroxyde contenant au moins deux atomes d'oxygène liés (-O-O-). Pour réaliser cette oxydation, une matière de départ A comprenant le composé organique et une matière de départ B comprenant le peroxyde sont continuellement mélangés l'une avec l'autre. Un microréacteur (1) est alimenté par ce mélange réactionnel liquide. Ce microréacteur (1) comporte une multitude de canaux parallèles de réaction (4') adjacents à des canaux de refroidissement (3'). Le mélange réactionnel se trouve donc divisé dans les canaux réactionnels (4'). Les canaux de refroidissement (3') sont remplis d'un fluide caloporteur qui évacue la chaleur produite dans les canaux de réaction (4') du microréacteur (1). Le microréacteur (1) utilisé est caractérisé par le fait que la plus grande dimension a des canaux de réaction (4'), perpendiculaire à la direction du flux des canaux adjacents est < 1 000 .mu.m, de préférence < 500 .mu.m, et que la plus faible épaisseur b des parois entre les canaux de réaction (4') et les canaux de refroidissement (3') est < 1 000 .mu.m, de préférence < 100 .mu.m. On a pu montré qu'un microréacteur comportant plusieurs étages en série (10a... 10n), dont la section des canaux de réaction va en augmentant dans la direction du flux, est particulièrement utile pour réaliser cette oxydation. On utilise de préférence ce procédé pour l'oxydation de sulfures organiques, le peroxyde d'hydrogène étant alors utilisé comme agent oxydant.

(57) The organic compound is oxidized in the form of a solution by addition of a peroxidic oxidizing agent containing at least two linked oxygen atoms (-O-O-). For this purpose, a starting material A comprising the organic compound and a starting material B comprising the peroxidic oxidizing agent are continuously mixed with one another, then the liquid reaction mixture is fed to a microreactor (1) having an abundance of parallel reaction channels (4') and adjacent cooling channels (3') and thus simultaneously divided among the reaction channels (4'). The cooling channels (3') are charged with a coolant here to remove the heat generated in the microreactor (1) by the exothermic oxidation reaction in the reaction channels (4'). The microreactor (1) used for this purpose is characterized in that the largest channel dimension a of the reaction channels (4') perpendicular to the flow direction of the adjacent channels is < 1000 .mu.m, preferably < 500 .mu.m, and the lowest wall thickness b between the reaction channels (4') and the cooling channels (3') is < 1000 .mu.m, preferably < 100 .mu.m. A microreactor having a plurality of serial stages (10a... 10n) whose reaction channel cross-sectional areas increase in the flow direction, has proved particularly suitable. The process is preferably used for the oxidation of organic sulphides, hydrogen peroxide being used as oxidizing agent.

Le A 32 487 - Foreign countries BW/m/vos/W6/V11.08.1998

Process and apparatus for the oxidation of organic compounds in liquid phase using peroxidic oxidizing agents

Abstract

The organic compound is oxidized in the form of a solution by addition of a peroxidic oxidizing agent containing at least two linked oxygen atoms (-O-O-). For this purpose, a starting material A comprising the organic compound and a starting material B comprising the peroxidic oxidizing agent are continuously mixed with one another, then the liquid reaction mixture is fed to a microreactor (1) having an abundance of parallel reaction channels (4') and adjacent cooling channels (3') and thus simultaneously divided among the reaction channels (4'). The cooling channels (3') are charged with a coolant here to remove the heat generated in the microreactor (1) by the exothermic oxidation reaction in the reaction channels (4'). The microreactor (1) used for this purpose is characterized in that the largest channel dimension a of the reaction channels (4') perpendicular to the flow direction of the adjacent channels is $< 1000\ \mu m$, preferably $< 500\ \mu m$, and the lowest wall thickness b between the reaction channels (4') and the cooling channels (3') is $< 1000\ \mu m$, preferably $< 100\ \mu m$. A microreactor having a plurality of serial stages (10a ... 10n) whose reaction channel cross-sectional areas increase in the flow direction, has proved particularly suitable. The process is preferably used for the oxidation of organic sulphides, hydrogen peroxide being used as oxidizing agent.

Le A 32 487 - Foreign countries

Process and apparatus for the oxidation of organic compounds in liquid phase using peroxidic oxidizing agents

The present invention relates to a process and an apparatus for the oxidation of organic compounds in liquid phase, in which the organic compound is oxidized in the form of a solution by addition of a peroxidic oxidizing agent containing at least two linked oxygen atoms (-O-O-).

Material conversions in chemically reacting systems are accompanied by heats of reaction, which in the case of exothermic reactions lead to heat production. If the chemical reactions proceeding are rapid, the heat of reaction released per unit time is correspondingly large. Oxidation reactions of organic compounds in liquid phase in which peroxidic compounds are used as oxidizing agents are to be assigned to this type of reaction, i.e. they usually proceed rapidly, sometimes explosively and highly exothermically.

Peroxidic compounds are taken to mean here chemical compounds which have at least one O-O group consisting of two linked oxygen atoms. These compounds include both inorganic (e.g. hydrogen peroxide, sodium perborate) and organic peroxidic compounds (e.g. peroxides, hydroperoxides, peracids). They are termed below simply peroxides or peroxidic compounds.

A priority object of the reaction technologist is, in the case of chemical reactions proceeding highly exothermically with the use of peroxidic compounds, to conduct the course of the reaction in a temperature controlled manner, i.e. to remove in a controlled manner the heat of reaction released per unit time by heat transfer, e.g. to limit the upper reaction temperature, to prevent an explosive course of the reaction or to set a desired reaction temperature which is optimum for the process. In many cases, an isothermal reaction procedure is sought-after here, avoiding temperature peaks. Temperature peaks frequently occur at the start of the reaction owing to the high concentrations of starting material and, resulting therefrom, owing to the high reaction rates. A controlled temperature procedure, avoiding excessive temperatures, is urgently required, especially when reactions are carried out with the use of peroxides, in order to suppress the decomposition of the thermally sensitive and comparatively expensive

peroxidic compounds. Thus, for example, the kinetic energy of activation of the unwanted decomposition reaction of hydrogen peroxide

$$H_2O_2 \Rightarrow H_2O + 0.5\ O_2$$

is 201 kJ/mol, i.e. high temperatures lead to a great acceleration of the unwanted, explosively proceeding decomposition reaction. It must therefore be ensured that the peroxide is not exposed, or is exposed only briefly, i.e. for seconds, to relatively high temperatures. Further advantages of a temperature-controlled reaction procedure are given, for example, by the reduction of unwanted secondary reactions of the reaction product obtained by oxidation with peroxides, especially if the unwanted secondary reaction proceeds with a higher energy of activation than the desired main reaction. As a result, starting materials and residual materials can be minimized, which leads to processes which are substantially more sparing of the environment and resources.

From the requirement to conduct reactions using peroxidic oxidizing agents in a temperature-controlled manner, there results the object of providing a chemical reactor which has a sufficiently high heat transfer efficiency.

Liquid phase reactions which proceed highly exothermically with the use of peroxidic compounds are usually carried out in the prior art in stirred tanks or in reaction apparatuses having stirred-tank characteristics, such as loop reactors [1]. A distinction must generally be made here between a continuous mode of operation and semibatch mode of operation. The pure batch mode of operation is rather unusual. Continuously operated stirred tanks are characterized in that the concentrations of the reactants are low owing to the back-mixing. In the steady state and with ideal back-mixing, the concentrations in the reactor are known to correspond to the concentrations at the reactor outlet. As a result, the reaction course is correspondingly slow and the heat can be removed in a controlled manner via the stirred-tank wall or heat exchanger internals.

In the semibatch operation, usually one reaction component, generally the peroxidic compound, is added to the reagents present in the stirred tank (fed batch process). This mode of operation is typical in multiproduct plants for preparing fine chemicals [2]. The peroxide is added slowly, generally over many hours, so that the heat of reaction

released in the chemical reaction can be removed in a controlled manner via the heat transfer surfaces and a defined, not excessive temperature, can be set in the stirred tank.

A disadvantage in the conventional continuous or semibatch mode of operation is the low reactor efficiency, i.e. the low production rate per unit volume and time. In many cases this results in undesirably large reactors or a multiplicity of units connected in parallel which give rise to relatively high capital and operating costs. Further disadvantages result from yield and selectivity losses owing to the long reactor residence times and owing to the broad residence time spectra. Since, in the case of highly exothermic liquid-phase reactions with the use of peroxides, large amounts of heat must be removed, the coolant must frequently be kept at a very low temperature, so that relatively high temperature gradients between stirred-tank contents and stirred-tank wall occur. This promotes the formation of deposits on the heat transfer surfaces, e.g. as a result of crystallization, and increases, as a result, the cleaning expenditure required. The scale-up of a stirred tank, in the event of a process development or with increase of the production capacity, is further made more difficult by the ratio of heat transfer surface area to stirred-tank volume becoming smaller with increasing stirred-tank size. Frequently, in such cases, this is coped with by the reaction mixture being circulated by pumping in an external liquid circuit and a large part of the heat of reaction being removed in a heat exchanger disposed in the circuit.

The said disadvantages may, in the case of liquid-phase oxidations of organic compounds using peroxides as oxidizing agent, be avoided or at least reduced by means of the fact that the reaction is carried out continuously and substantially free of back-mixing in the flow tube or reactors having flow-tube characrteristics. It is known that reactions can be carried out therein, depending on the underlying reaction equation, with relatively high yield and selectivity, e.g. in the case of oxidations proceeding partially, in short reaction times, and therefore with high space-time yields. From the safety aspect, the low holdup in such reactors is advantageous. The technical implementation of highly exothermic liquid-phase reactions with peroxides in conventional reactors having flow-tube characteristics, such as a double tube or tube-bundle reactor, has failed hitherto because the reaction, owing to the higher concentration level of the reaction components, proceeds markedly more rapidly than in stirred tanks and thus the heat of reaction released per unit time in many cases can no longer be removed reliably and in a controlled manner. The insufficient heat removal

leads to overheating and, in the extreme case, to an explosive decomposition of the thermally sensitive peroxides.

To utilize the potential for improvement described for reactors having flow-tube characteristics when carrying out liquid-phase oxidations using peroxidic compounds as oxidizing agents, an important object is to use novel reactor systems which have a heat-transfer efficiency higher than conventional reactors by at least a factor of 10 to 100.

This object is achieved according to the invention by means of the fact that a starting material stream A comprising the organic compound and a starting material stream B comprising the peroxidic oxidizing agent are continuously mixed with one another and the liquid reaction mixture is fed to a microreactor having an abundance of parallel reaction channels and adjacent cooling channels and is thus divided among the reaction channels. At the same time, the cooling channels are charged with a coolant to remove the heat generated in the microreactor by the exothermic oxidation reaction in the reaction channels. The microreactor used for this purpose is characterized in that the largest channel dimension a of the reaction channels perpendicular to the flow direction of the adjacent channels is < 1000 µm, preferably < 500 µm, and the lowest wall thickness b between the reaction channels and the cooling channels is < 1000 µm, preferably < 100 µm.

Advantageously, the reaction channels here have a hydraulic channel diameter d < 1000 µm, preferably < 500 µm.

Preferably, this process is used for the oxidation of organic sulphides, i.e. the compound to be oxidized consists of an organic sulphide.

The process according to the invention has proved to be particularly useful for the oxidation of 3,5-dithio-heptane-1,7-diol diacetate. As peroxidic oxidizing agent here, use is made of hydrogen peroxide.

Other reactions particularly suitable for the use of the process according to the invention have proved to be the oxidative cleavage of olefins to form carboxylic acids, with the use of hydrogen peroxide, in particular using sodium tungstate as catalyst, the

oxidation of ketones to give carboxylic esters in accordance with Baeyer-Villiger and the oxidation of thiols to sulphonic acids, using hydrogen peroxide as oxidizing agent.

To produce the reaction mixture comprising the organic compound and the peroxidic oxidizing agent, advantageously, a jet mixer is used, in which one starting material is injected into the other.

According to a particular embodiment, the reaction mixture is transported through a tubular reactor which is upstream of the microreactor and has a residence time of 10 ms to 20 s, preferably 10 ms to 10 s. In this case, use can be made of the advantageous variant where the reaction is carried out in the tubular reactor under adiabatic conditions and the hot reaction mixture is cooled down by more than 20°C in the microreactor within 1 ms to 10 s, preferably within 1 ms to 1 s. In this manner, a considerable increase in selectivity can be achieved.

According to a further development of the process according to the invention, the reaction mixture is transported through a plurality of microreactors connected in series one after the other. Advantageously in this case, the reaction channel cross-sectional area increases in the flow direction.

There is the possibility here that between the microreactors, or between the jet mixer and the microreactor, starting materials A, B or circulated reaction mixture are fed in at one or more points.

An apparatus suitable for carrying out the process according to the invention consists of a mixer for the continuous mixing of at least two starting material streams A, B and a downstream microreactor having reaction channels and cooling channels, where the largest channel dimension a of the reaction channels perpendicular to the flow direction of the adjacent channels is < 1000 µm, preferably < 500 µm and the lowest wall thickness b between the reaction channels and the cooling channels is < 1000 µm, preferably < 100 µm. According to the invention, the microreactor is serially subdivided here into at least two microreactor stages whose reaction channel cross-sectional areas increase stepwise in the flow direction.

According to a preferred design, the reaction channels of the reactor stages connected in series one after the other have a hydraulic channel diameter d < 1000 µm, preferably < 500 µm.

Of advantage here is a circulation for the reaction mixture or the feed of fresh starting material between one or more microreactor stages.

According to a preferred embodiment, an adiabatic tubular reactor is disposed between the mixer and the microreactor stages.

By means of the invention, the following advantages are achieved, compared with the conventional stirred-tank mode of operation:

Owing to the controlled temperature procedure and owing to the short residence times of the reaction mixture in the microreactor, higher yields in liquid-phase reactions may be achieved. The losses due to decomposition of the peroxidic oxidizing agent are reduced. The space-time yields can be significantly increased in comparison with conventional modes of operation. Thus, the reaction running times for the preparation of a defined amount of product when continuously charged microreactors are used can be decreased from hours to minutes. Furthermore, the expenditure on cleaning can be reduced, e.g. by simple flushing of the apparatus. This, and the possibility of a simpler automation of the process sequence, can greatly reduce the production costs. Further advantages result from higher, reproducible product qualities and the lower reactor hold up relevant to safety.

Owing to the high heat transfer coefficients in the microreactor, in many applications, instead of a complex refrigeration circuit (e.g. brine, ammonia, Freon 12), a cooling water circuit can be used. This leads to savings in energy requirements. Owing to the small size of the microreactor and the relatively low procurement costs in comparison with stirred-tank reactors, a plurality of microreactors can be connected together, e.g. to increase the throughput rates, or can be exchanged for differently constructed or new microreactors. It is also conceivable that the microreactors are replaced after a certain service life as "disposable reactors".

The invention is described in more detail below with reference to drawings and exemplary embodiments.

In the drawings

Fig. 1	shows the basic structure of a microreactor
Fig. 2	shows a diagrammatic flow chart of a plant for carrying out the process according to the invention
Fig. 3	shows a cross-section through a jet mixer
Figs. 4a-4c	show various designs of microreactor stages connected in series one after another and
Fig. 5	shows two micoreactors connected one after the other with an intermediate tubular reactor.

Microheat exchangers are described, for example, in [3] (DE 37 09 278) or in [4] (US 4 516 632). In [5], the use of such, or similarly constructed, microheat exchangers as chemical microreactors is described in general form. To illustrate the mode of functioning of such a microheat exchanger, Fig. 1 shows, by way of example, the structure of the microheat exchanger 1 described in [3]. This consists of a stack of diffusion-welded metal foils 2 having foil thicknesses of, for example, 100 µm. Into these metal foils, using tools ground to shape, there are introduced microchannels 4' running parallel to one another for a reaction mixture 4 and microchannels 3' for a coolant 3. The minimum channel dimensions which can be achieved in [3] are in the region of 10 µm. The geometrical shape of the microchannels 3' and 4' can be selected as desired. Thus, for example, rectangular and circular cross-sections are possible. The microchannels 3' and 4' can have different dimensions. In order to ensure streams of equal flow rate in the individual microchannels of a fluid passage, the microchannels of a fluid passage are identical to one another. The characteristic hydraulic channel diameter of microchannels of the fluid passage i (here: i = 3 or 4) is given by the relationship

$d_i = 4\ A_i/U_i$, where

d_i = characteristic hydraulic channel diameter of the fluid passage i

A_i = flow-bearing channel cross-sectional area of the fluid passage i

U_i = wetted channel periphery of the fluid passage i

i = index for the fluid passage (number of fluid passages ≥2)

Fig. 1 likewise shows, as an enlarged detail, a microchannel 4' of the fluid passage 4 having the channel dimension a_4, where a_4 is the largest dimension of the microchannel 4' perpendicular to the flow direction of the coolant passage 3. Furthermore, the lowest wall thickness b_4, i.e. the lowest distance between the two fluid passages 3 and 4 is indicated.

Microreactors are here generally characterized in that either

- the characteristic hydraulic channel diameter d_i (here: i = 3 and 4)
 or
- the channel dimension a_i (in the reaction channels)

of all microchannels of at least one fluid passage i are less than 1000 μm. The lowest wall thickness b_i between the individual fluid passages is likewise to be selected less than 1000 μm, preferably less than 100 μm. These statements also apply when the microchannels of a fluid passage i are different sizes from one another.

The individual metal foils, in the example of Fig. 1, are stacked one above the other in such a manner that the microchannels of two adjacent fluid passages run at 90° to one another (cross-flow microheat exchanger) and are sealed off from one another helium-tightly. When the microheat exchanger is used as a chemical microreactor, one fluid passage is used for conducting the flow of the reaction mixture 4, and the other fluid passage is used for conducting the flow of the coolant 3. In addition to the cross-flow arrangement shown in Fig. 1, other typical flow arrangements such as co-current flow and counter-current flow and all combinations thereof can also be implemented, however. The marked increase in heat transfer efficiency in the microreactor is based on the fact that due to the small hydraulic channel diameter d_i, but especially due to the small channel dimensions $a_{i,}$, the transport paths for the heat flows to be transferred between the fluid passages are very short. In comparison with heat transfer coefficients of approximately 1000 W/m^2 K in conventional reactors (liquid on the reaction side and coolant side), values of the order of magnitude of 20,000 W/m^2 K are achieved in microreactors (both fluid passages: d_i = 80 μm, a_i = 100 μm, water). The specific heat transfer surface area can reach values greater than 100 cm^2/cm^3 in comparison with

approximately 1 cm^2/cm^3 in conventional tube-bundle reactors. This results in total in an increase of the volume-specific heat transfer efficiency by a factor of at least 1000.

Fig. 2 shows a preferred plant for carrying out highly exothermic liquid-phase reactions using peroxides as oxidizing agent and using microreactors to remove the heat of reaction. At least two starting material streams 6a and 6b (in the general case m starting material streams 6a to 6m) are fed from separate starting material reservoir vessels 5a and 5b via transport means 7a and 7b and optionally via filter elements 8a and 8b to a mixing unit 9. At least one of the starting material streams comprises the peroxidic compound or a precursor form, from which the peroxidic compound is formed by reaction in situ. To mix the reaction components, preferably, rapidly mixing apparatuses are used, for example the jet mixer 9 shown in Fig. 3. The feed of 6a and 6b can also be interchanged. The mixing times of such jet mixers are in the order of milliseconds. After mixing is complete, the reaction mixture enters directly into the microreactor 10. In order that as large a part as possible of the reaction proceeds under temperature control with cooling using a coolant 11, or excessive temperatures do not occur prior to entry into the microreactor, the residence time between mixing unit 9 and microreactor 10 must be selected to be short. Care must be taken to ensure uniform flow into the microreactor. The residence time in the microreactor 10 is typically in the range between 1 ms and 20 s.

A variant allows a tube section 13a having a residence time of 10 ms to 20 s, preferably 10 ms to 10 s, to be connected between mixing unit 9 and microreactor 10, so that the reaction mixture heats independently to reaction temperature, owing to the heat of reaction released prior to entry into the microreactor 10. A further variant which can be derived from Fig. 2 is that a defined number of microreactors are connected in parallel to increase the throughput performance. When the reaction is complete, the product mixture exiting from 10 is fed via a further tube section 13b to a product collection vessel 12.

Optionally, one or more conventional heat exchangers can also be connected downstream of the microreactor 10 to remove residual heat. By continuously charging the starting material reservoir vessel and emptying the product collection vessel, if required, continuous operation of the apparatus can be maintained even over relatively long periods of time. Continuous operation can also be achieved by the use of a

continuously operating belt filter for product work-up, instead of the collection vessel 12.

By serial connection of two or more, but preferably less than 20, because of the required connection complexity, identical or differently constructed microreactors, a particularly advantageous temperature profile with respect to yield and selectivity of the reaction can be achieved. Fig. 4a shows the serial connection of a plurality of microreactors 10a to 10n, the individual microreactors optionally being connected to one another without intermediate spaces, that is directly, or via a plurality of tube sections 13a to 13n. In general, a cascade of conventional heat exchangers can be connected downstream of the last microreactor 10n. The coolant streams 11a to 11n can be connected in series to and/or parallel to one another. Typically, a coolant circuit is installed, where the coolant streams 11a to 11n are linked in series to one another. Alternatively, it is possible to operate a plurality of coolant circuits operated independently of one another. In addition to the cross-flow arrangement of the heat transport medium within the microreactor shown here, a counter-current, cross-counter-current, co-current or cross-co-current flow arrangement or all combinations thereof can also be achieved. To set identical temperature profiles along the microchannels of a fluid passage, a co-current or counter-current flow arrangement is frequently to be preferred to the cross-flow arrangement.

Fig. 4b and Fig. 4c show, for clarification, two of a plurality of possible circuit variants of the coolant. Fig. 4b shows a cross-co-current flow arrangement having a coolant circuit 11, in which the microreactors 10a to 10c are connected to one another directly. Fig. 4c illustrates a cross-counter-current flow arrangement of the coolant 11a and a simple cross-flow arrangement of the coolant 11b in a second cooling circuit. The individual microreactors 10a to 10c are connected to one another via uncooled tube sections 13a to 13c. In the region of the uncooled intermediate tube sections 13a to 13c in Fig. 4c, the reaction proceeds approximately adiabatically with temperature increase. The reaction mixture is cooled down downstream of each tube section in the microreactor, so that overall a sawtooth-like temperature profile results. The advantage of such a circuit is that the required microreactor volume can be reduced, which is advantageous especially in the case of reactions having reaction times in the region of greater than approximately 3 seconds. The pressure drops caused by wall friction in the

microchannels of the microreactor, especially in the case of high-viscosity fluids, are reduced by a circuit of this type.

For further reduction of the pressure drops, the microchannel dimensions can be adapted to the chemical heat production which changes in the course of the chemical reaction. Generally, chemical reactions proceed in such a manner that the chemical reaction is rapid at the start and has a high heat production per unit time. Therefore, the microchannel dimensions must be small at the start of the reaction in order to ensure sufficiently high heat transfer efficiency. With advancing conversion, the reaction generally becomes slower and the microchannel dimensions can be chosen to be correspondingly larger. The equipment circuit resulting herefrom is made in accordance with Figs. 4a to 4c, the channel dimensions of the individual microreactors being larger in the flow direction of the reaction mixture.

Between the individual microreactors in Fig. 4a, optionally, fresh starting material solutions 14j (j = a to n) or circulated reaction mixture or product solution 15 (j_1/j_2) (j_1 = b to (n+1), j_2 = a to n) can be fed in at one or more points. Thus, for example, a portion of the required amount of peroxide can be added via the jet mixture, and the remainder as partial stream 14c between the microreactors 10b and 10c. This has the advantage that the peroxide concentration in the reaction mixture is kept low and decomposition of the peroxide is suppressed.

A preferred microreactor circuit is shown in Fig. 5. Two series-connected microreactors 10a and 10b are separated from one another by a tube section 13b. In the first microreactor 10a, the heat of reaction released immediately after the mixing in 13a, and that released in 10a, is removed under control. In this case, the microreactor 10a ensures a controlled and selective reaction procedure at the start of the reaction. This is of importance precisely at the start of the reaction, since here, high starting material concentrations are still present, and, in association therewith, a high reactivity. The residual conversion, with a generally lower heat production per unit time, proceeds in the downstream tube section 13b. The residual heat released in this case is removed in a second microreactor 10b. The second microreactor 10b has, in this case, the additional function of a safety heat exchanger which cools the reaction mixture to low temperatures, so that no significant reaction conversions can proceed any longer downstream of this unit, i.e. significant reaction in the downstream product reservoir 12

cannot occur. Optionally, via a bypass circuit, one portion of the coolant 11a can be conducted through the microreactor 10b, and the other portion 11b can be conducted past the microreactor 10b in the bypass. In the mixing point 14, the preheated coolant stream 11a and the cold stream 11b are combined. In this case, the temperature of the coolant stream 11c can be set variably.

A further reaction procedure implemented is shown in Fig. 6. After mixing the reactants in the mixing unit 9, the reaction first proceeds adiabatically in an uncooled tube section 13a. After complete reaction or partial reaction of the reactants has been performed, the hot reaction mixture is cooled down in a microreactor 10 spontaneously within milliseconds to lower temperatures. The reaction can proceed further in this case in 10 or on being cooled down comes to a stop. Thus, unwanted side reactions, such as the thermally related decomposition of peroxide or other secondary reactions can be suppressed. A reaction procedure variant in which the reaction proceeds up to a partial conversion, at which high selectivity is achieved, in tube section 13a and is then stopped by spontaneous cooling in the microreactor 10 is typical.

In addition to the described liquid-phase oxidation using peroxides as oxidizing agent, the apparatuses described in Figs. 2 to 6 are also suitable for use in standard form for carrying out other rapidly proceeding, highly exothermic liquid-phase and gas-phase reactions.

Fields of application of the process described here and of the apparatuses shown in Figs. 2 to 6 are firstly in the field of chemical production, but secondly also in the field of process development (process optimization, parameter studies, kinetic studies, development and screening of novel process concepts).

Exemplary embodiments

Example 1

In an experimental apparatus according to Fig. 2, the homogeneously catalyzed liquid-phased oxidation of the organic disulphide 3,5-dithio-heptane-1,7-diol diacetate to the corresponding disulphone using hydrogen peroxide as oxidizing agent and using a microreactor was studied.

For this reaction, there is the following overall reaction equation:

$$CH_3\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}S\text{-}CH_2\text{-}S\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}CH_3 + 4H_2O_2 \Rightarrow$$
$$CH_3\text{-}CO\text{-}O\text{-}CH_2\text{-}CH_2\text{-}SO_2\text{-}CH_2\text{-}SO_2\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CO\text{-}CH_3 + 4H_2O$$

The highly exothermic and rapidly proceeding reaction proceeds in this case via the sulphoxide or disulphoxide stage to the sulphone or disulphone. The heat of reaction per mole of formula conversion is 1100 kJ. As homogeneous catalyst, use is made of sodium tungstate.

The chief problem in the reaction carried out conventionally in a semibatch procedure is heat removal (see also [1]). In this case, the oxidizing agent H_2O_2 can only be added slowly to the amount of disulphide already present. To prepare product solution on an m^3 scale, in this case, depending on the size of the stirred tank used, a dosage period of more than 20 hours is necessary, which requires relatively high expenditure of time, of personnel and of safety. The disulphone yield, based on disulphide used, is 75%.

In the case of the continuous charging of the microreactor in accordance with Fig. 2, 3.79 kg of the disulphide are placed in the reservoir 5a together with 15.75 kg of acetic acid at 20°C. 6.4 kg of 35% strength hydrogen peroxide solution are placed in the reservoir 5b together with 299 g of water and 99 g of sodium tungstate, likewise at 20°C. The two starting material streams 6a (disulphide solution) and 6b (hydrogen peroxide solution) are fed via two gear pumps 7a and 7b in a ratio of 2.8:1 to the mixing unit 9 in accordance with Fig. 3. Immediately after the mixing in 9, the reaction starts. The total throughput is 36.7 kg/h. The residence time in the uncooled tube section 13a between mixer 9 and microreactor 10 is 3.3 seconds. In this case, the

mixture heats from 20°C to 113°C immediately at the entrance to the microreactor 10. The use of a tube section upstream of the microreactor has the advantage that the reaction mixture heats to higher reaction temperatures independently. The microreactor used has a cross-flow arrangement with respect to reaction and coolant passage. The residence time of the reaction mixture in the microreactor is 1.1 seconds. The exit temperature of the reaction mixture from the microreactor is 37°C. 34.2 kg/h of the cooling water 11 are passed through the microreactor in cross-flow to the reaction mixture. The cooling water inlet temperature is 12°C, the exit temperature 56°C. The residence time of the cooling water in the microreactor is 1.2 seconds. The hydraulic channel diameter d in accordance with equation 1 is 160 µm for both fluid passages, the channel dimensions a in accordance with Fig. 1 perpendicular to the flow direction of the adjacent fluid passage are 140 µm in each case. After exit from the microreactor, the reaction mixture passes through an uncooled tube section 13b to the inlet into the product reservoir vessel 12. The residence time between microreactor 10 and entry into the product reservoir 12 is 24.5 seconds. In this case, the reaction mixture heats from 37°C to 49°C owing to the residual reaction. The product mixture is then passed into the product reservoir 12 and prepared for analysis.

The product yield of disulphone achieved in this manner, based on disulphide used, is 76.2% at very good product quality. In comparison with a conventional semibatch procedure, the space-time yield is increased by a factor greater than 4.

Example 2

With a procedure modified with respect to Example 1, 99 g of sodium tungstate are made up with 299 g of water in a separate third starting material reservoir vessel (not shown) and are continuously mixed immediately upstream of the mixer 9 with the 35% strength hydrogen peroxide solution 6b in a ratio of 0.06:1. In comparison with the above described procedure, this has the advantage that, in the reservoir vessel 5b, no decomposition, due to the action of sodium tungstate, of the hydrogen peroxide placed therein occurs. The disulphone yield achieved corresponds to that in Example 1.

Example 3

In an experimental apparatus in accordance with Fig. 4a having two microstructure heat exchangers connected in series, a tube section between the heat exchangers 13b of 144 cm and coolant streams connected in parallel, the homogeneously catalysed liquid-phase oxidation of the organic disulphide 3,5-dithio-heptane-1,7-diol diacetate to the corresponding disulphone was carried out.

In the continuous charging of the microreactor, 5.33 kg of disulphide are dissolved in 8.76 kg of acetic acid (starting material stream 6a) and 5.13 kg of hydrogen peroxide (35% strength), 40 g of sodium tungstate and 119 g of water (starting material stream 6b) are mixed in the mixing unit 9 in a ratio of 2.7 to 1 and are fed into the reactor at a throughput rate of 37.62 kg/h, based on the entire reaction mixture. The residence time in the uncooled tube section between mixer 9 and microreactor is 1.2 seconds. In this case, the mixture heats from 20°C to 96°C. In the first microstructure heat exchanger 10a, the reaction mixture is cooled to 76°C, heats in the tube section 13b to 123°C and is cooled in the heat exchanger 10b to 57°C. The hydrodynamic residence time between mixing jet 9 and the second microstructure heat exchanger 10b is 14 seconds. The inlet temperature of the cooling water into the first microstructure heat exchanger 10a is 24.4°C, and the exit temperature 51°C at a throughput rate of 80.3 kg/h. The inlet temperature of the cooling water into the second microstructure heat exchanger 10b is 24.4°C, and the exit temperature is 70°C at a throughput rate of 42.5 kg/h. The product stream is then passed into the product reservoir without further temperature increase.

The product yield achieved in this manner, based on disulphide used, is 88.2% of theory.

The advantage of the reaction procedure having two series-connected heat exchangers, in comparison with the reaction procedure having one heat exchanger, is the higher disulphone yield based not only on disulphide, but also on hydrogen peroxide, and the higher starting material concentration which can be achieved in this procedure, which leads to a higher space-time yield.

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[3] DE 37 09 278 C2

[4] US 4 516 632

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for oxidizing an organic compound in a liquid phase, in which the organic compound is oxidized in the form of a solution by addition of a peroxidic oxidizing agent containing at least two linked oxygen atoms (-O-O-), characterized in that a starting material stream A comprising the organic compound and a starting material stream B comprising the peroxidic oxidizing agent are continuously mixed with one another and the liquid reaction mixture is fed to a microreactor having an abundance of parallel reaction channels and adjacent cooling channels and is thus divided among the reaction channels and in that the cooling channels are simultaneously charged with a coolant to remove the heat generated in the microreactor by the exothermic oxidation reaction in the reaction channels, where the largest channel dimension a of the reaction channels perpendicular to the flow direction of the adjacent channels is < 1,000 µm, and the lowest wall thickness b between the reaction channels and the cooling channels is < 1,000 µm.

2. A process according to claim 1, wherein the largest channel dimension a is < 500 µm and the lowest wall thickness b is < 100 µm.

3. A process according to claim 1 or 2, wherein said reaction channels have a hydraulic channel diameter d < 1,000 µm.

4. A process according to claim 1 or 2, wherein said reaction channels have a hydraulic channel diameter $d < 500$ µm.

5. A process according to any one of claims 1 to 4, wherein the starting material A is an olefin for oxidative cleavage, a ketone for conversion according to Baeyer-Villiger or a thiol for oxidation.

6. A process according to any one of claims 1 to 5, wherein the organic compound to be oxidized is an organic sulphide.

7. A process according to claim 6, wherein the organic sulphide is 3,5-dithio-heptane-1,7-diol diacetate.

8. A process according to any one of claims 1 to 7, wherein the peroxidic oxidizing agent is hydrogen peroxide.

9. A process according to any one of claims 1 to 8, wherein, to produce the reaction mixture comprising the organic compound and the peroxidic oxidizing agent, a jet mixer is used, in which one starting material is injected into the other.

10. A process according to any one of claims 1 to 9, wherein the reaction mixture is transported through a tubular reactor which is upstream of the microreactor and has a residence time of 10 ms to 20 s.

11. A process according to any one of claims 1 to 9, wherein the reaction mixture is transported through a tubular

reactor which is upstream of the microreactor and has a residence time of 10 ms to 10 s.

12. A process according to claim 10 or 11, wherein the reaction is carried out in the tubular reactor under adiabatic conditions and the hot reaction mixture is cooled down by more than 20°C in the microreactor within 1 ms to 10 s.

13. A process according to claim 10 or 11, wherein the reaction is carried out in the tubular reactor under adiabatic conditions and the hot reaction mixture is cooled down by more than 20°C in the microreactor within 1 ms to 1 s.

14. A process according to any one of claims 1 to 13, wherein the reaction mixture is transported through a plurality of microreactors connected in series one after the other.

15. A process according to claim 14, wherein the reaction channel cross-sectional area of the microreactors increases in the flow direction.

16. A process according to claim 9, wherein starting materials A, B or circulated reaction mixture, are fed in at one or more points between the jet mixer and the microreactor.

17. A process according to claim 14 or 15, wherein starting materials A, B or circulated reaction mixture, are fed in at one or more points between the microreactors.

18. An apparatus for carrying out a process according to any one of claims 1 to 17, comprising a mixer for the continuous

mixing of at least two starting material streams A, B and a downstream microreactor having reaction channels and cooling channels, where the largest channel dimension **a** of the reaction channels perpendicular to the flow direction of the adjacent channels is < 1,000 µm, and the lowest wall thickness **b** between the reaction channels and the cooling channels is < 1,000 µm, characterized in that the microreactor is serially subdivided into at least two microreactor stages whose reaction channel cross-sectional areas increase stepwise in the flow direction.

19. An apparatus according to claim 18, wherein the largest channel direction **a** is < 500 µm and the lower wall thickness **b** is < 100 µm.

20. An apparatus according to claim 18 or 19, wherein the reaction channels have a hydraulic channel diameter **d** < 1,000 µm.

21. An apparatus according to claim 18 or 19, wherein the reaction channels have a hydraulic channel diameter **d** < 500 µm.

22. An apparatus according to any one of claims 18 to 21, wherein a circulation is provided for the reaction mixture or the feed of fresh starting material between one or more microreactor stages.

23. An apparatus according to any one of claims 18 to 22, wherein an adiabatic tubular reactor is disposed between the mixer and the microreactor stages.

Fetherstonhaugh & Co.,
Ottawa, Canada
Patent Agents

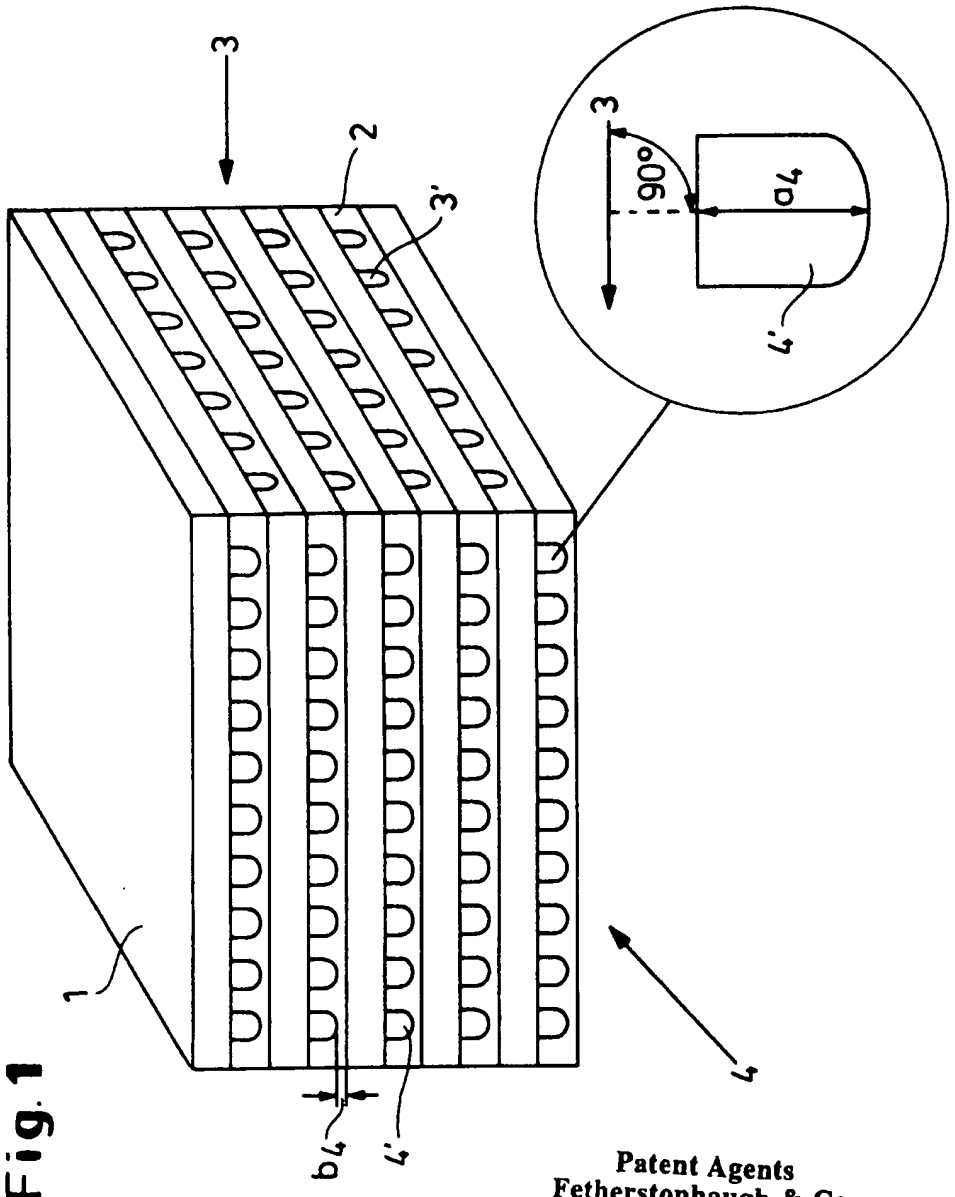


Fig.1

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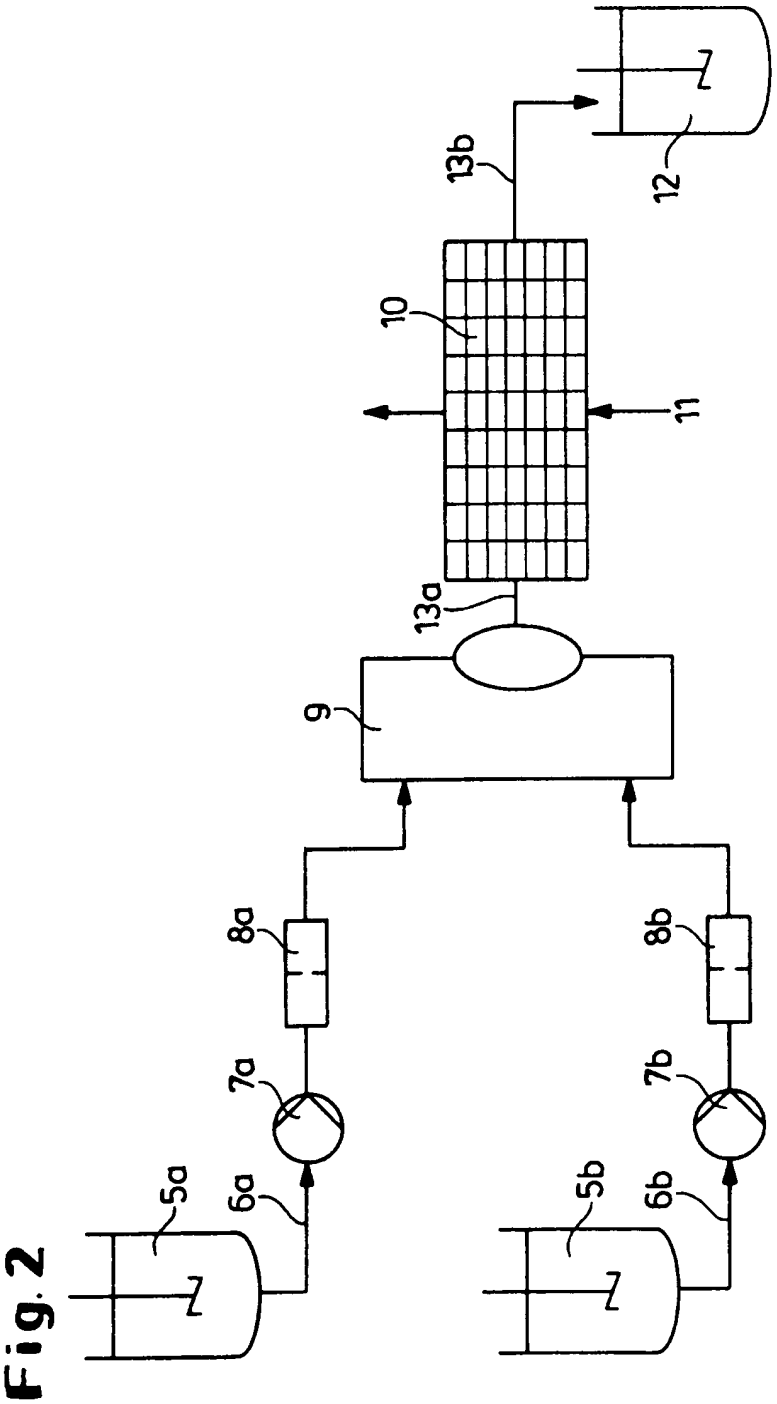


Fig. 2

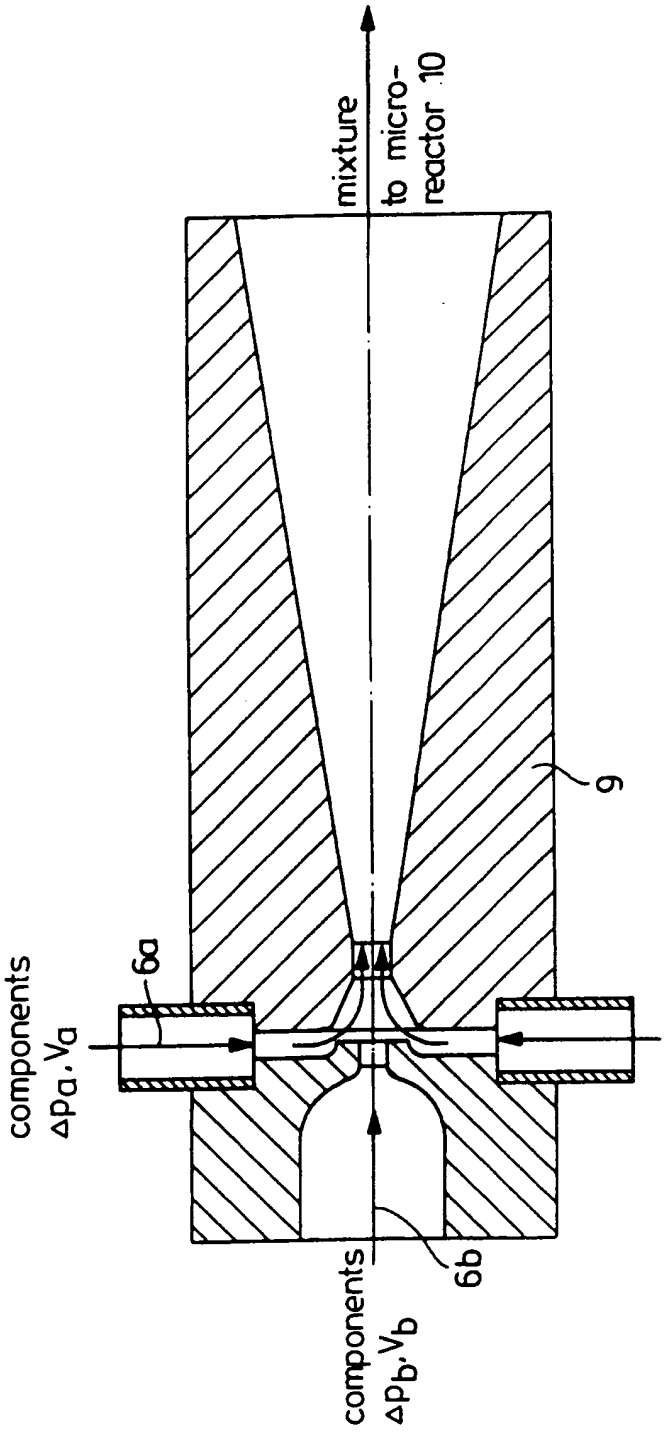

mixture
to micro-
reactor 10
9
components
Δpa, Va
6a
components
Δpb, Vb
6b

Fig. 3

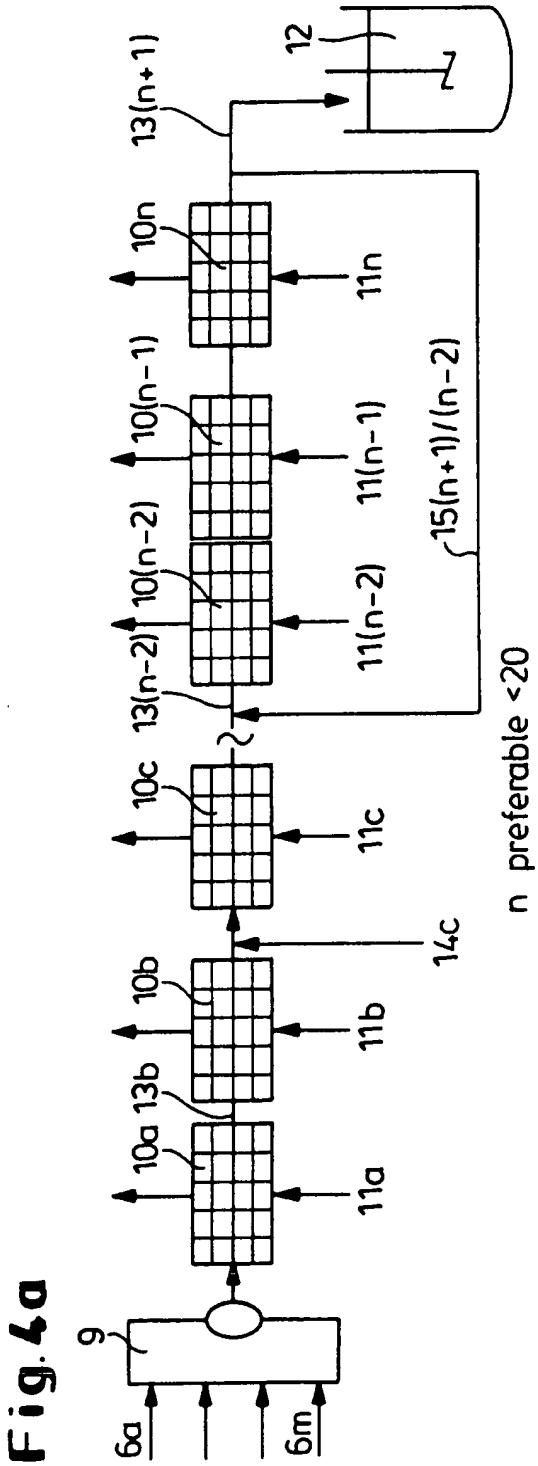

6a
6m
9
10a
13b
10b
11a
11b
14c
10c
11c
13(n-2)
10(n-2)
11(n-2)
10(n-1)
11(n-1)
15(n+1)/(n-2)
10n
11n
13(n+1)
12
n preferable <20

Fig.4a

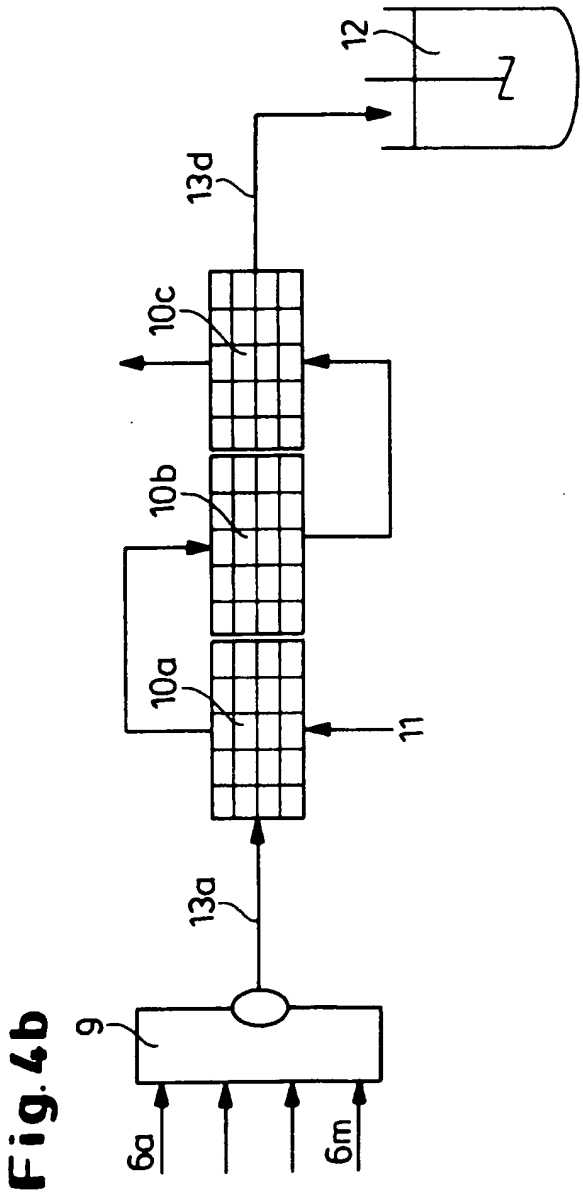


Fig.4b

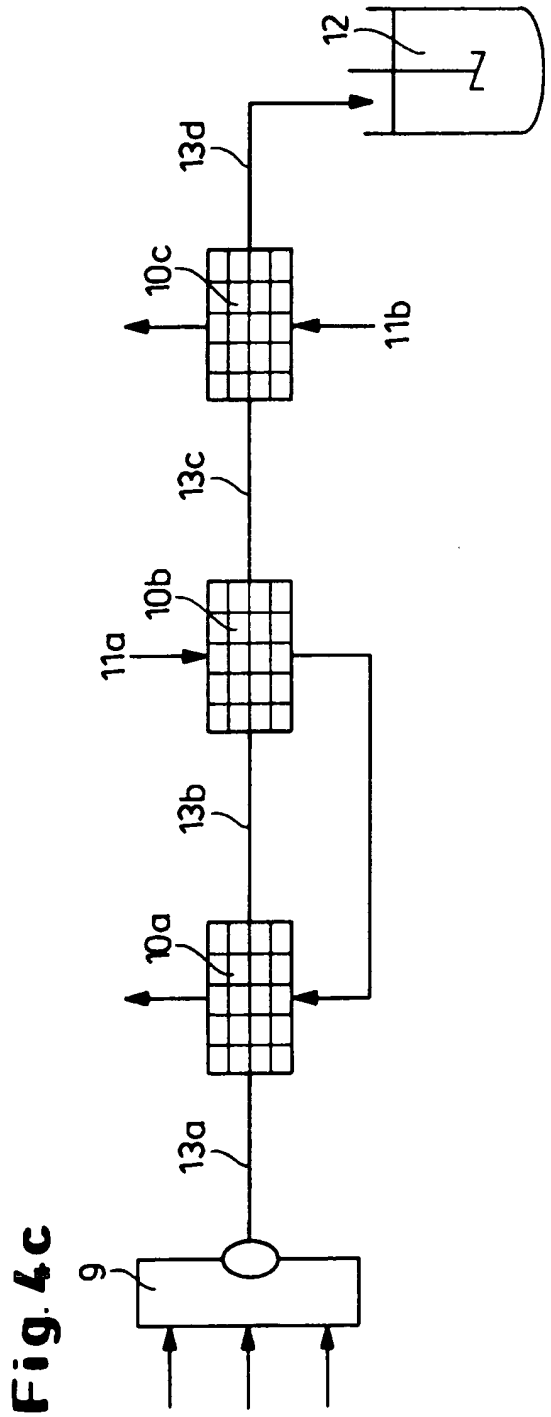


Fig.4c

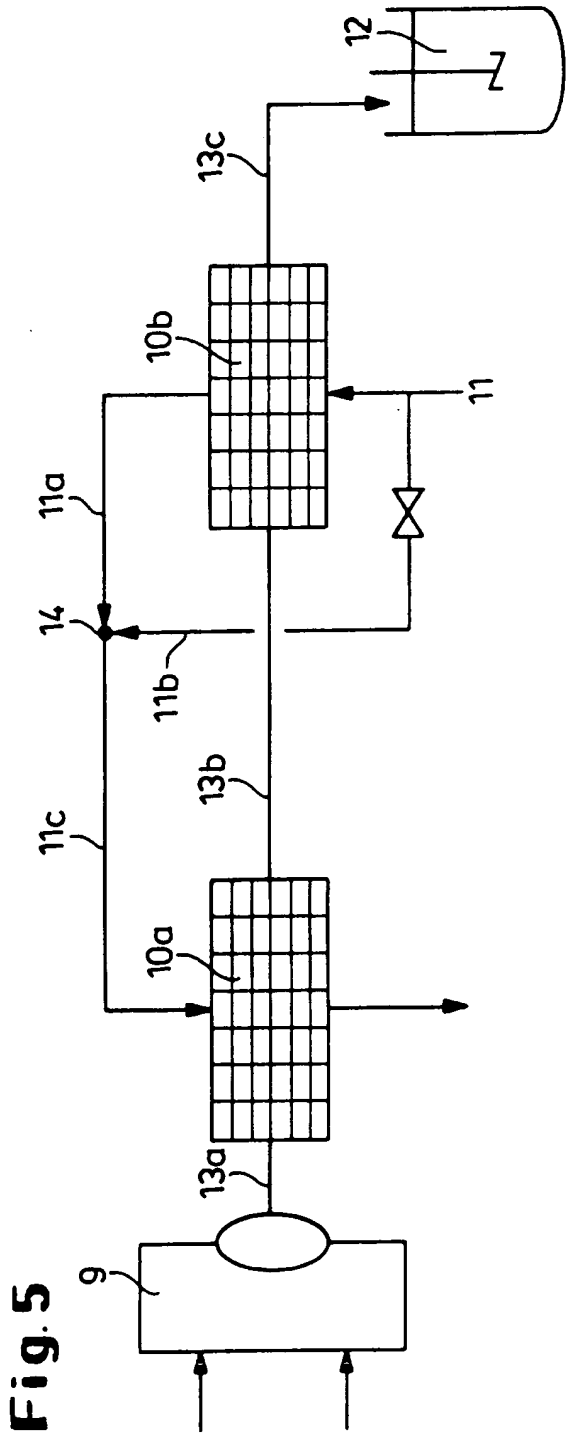


Fig.5

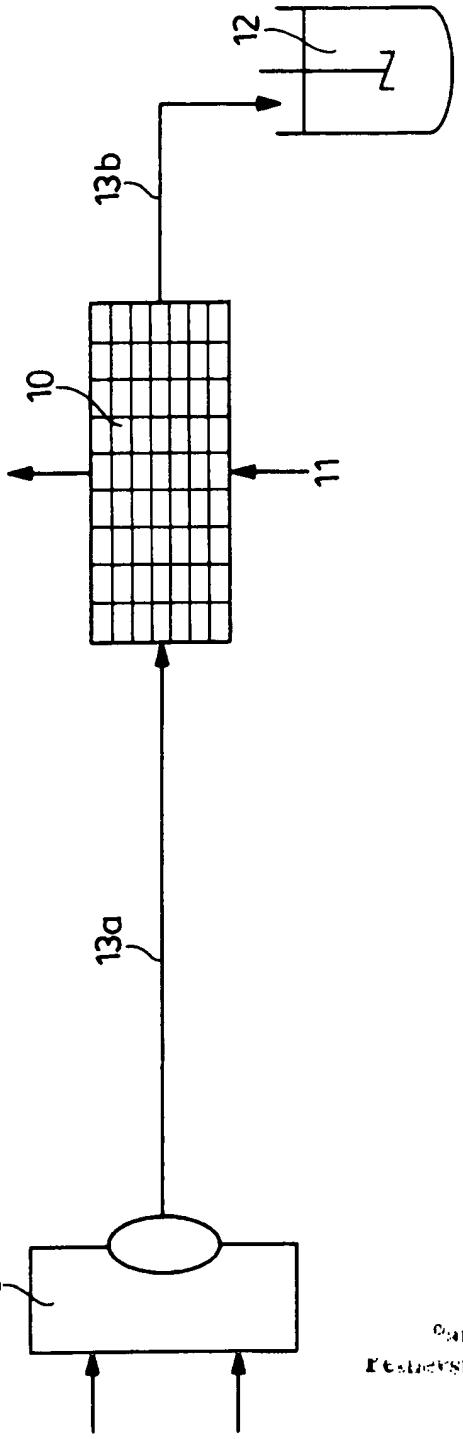


Fig.6

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